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THE NATURE OF THE PHASE TRANSITION OBSERVED FOR MONOLAYERS OF A--ETC(U)
OCT 81 D DAHLGREN, J C HENNINGER

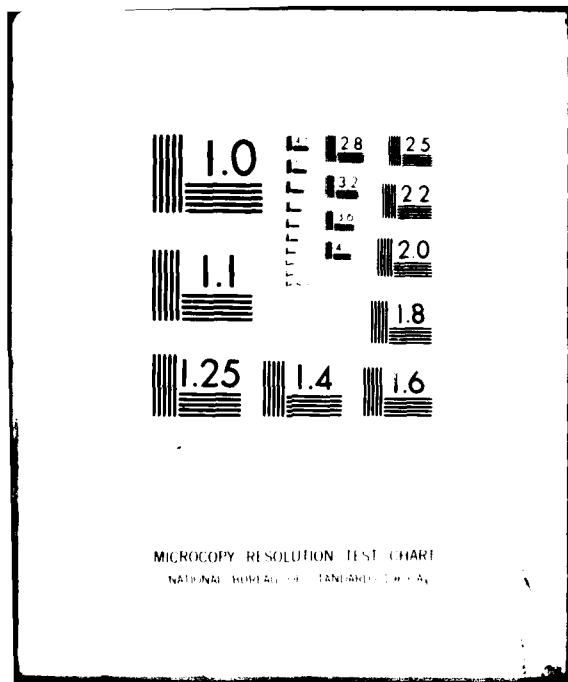
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The Nature of the Phase Transition Observed
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David Dahlgren and John C. Hemminger

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The Nature of the Phase Transition Observed
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Abstract

A model is presented for the reversible phase transition observed for azulene monolayers on Pt(111). Below the transition temperature the overlayer LEED pattern consists of (3x3) aligned with the substrate and (3x3) rotated by 30°. Above the transition temperature the LEED pattern is a (3x3) aligned with the substrate. The model attributes the phase transition to an order-disorder transition of the rotational orientation of azulene molecules with the molecular plane parallel to the surface.

Low energy electron diffraction and other surface sensitive probes have been used to observe many order transitions with temperature for chemisorbed molecular monolayers adsorbed on transition metal surfaces.¹ Unlike the cases of physisorbed overlayers these transitions invariably have been observed to be irreversible and in most cases are due to chemical modifications of the adsorbed molecule. Recently we reported the first observation of a reversible transition in the LEED pattern of a chemisorbed hydrocarbon monolayer adsorbed on a transition metal. The system is azulene ($C_{10}H_8$) chemisorbed on Pt(111).² In this communication we indicate that this transition can be ascribed to an order-disorder transition of the rotational orientation of molecules with the molecular plane parallel to the surface.

When azulene is adsorbed on Pt(111) at room temperature and at coverages which lead to C/Pt atom ratios (from Auger electron spectroscopy) in the range of $1 \leq C/Pt \leq 1.3$ the ordered overlayer of interest is obtained. Following formation of an overlayer in this coverage range the observed LEED pattern consists of a bright $1/3$ order ring. This indicates a well defined intermolecular spacing three times the Pt surface unit cell vector. Domains with random orientation with respect to the Pt surface lead to the ring pattern. If this overlayer is annealed at $\sim 125^\circ\text{C}$ an overlayer which exhibits a reversible temperature dependence is observed. Figure 1 shows the LEED pattern obtained from this overlayer below and above the transition temperature. There is no change in the Auger spectrum and no hydrogen evolu-

tion associated with the transition. The facts that the transition is reversible and the sample may be cycled through the transition many times with no change in the behavior of the LEED pattern is strong evidence that the transition is not associated with any chemical modification of the adsorbed azulene.

The LEED pattern obtained from the lower temperature phase (α -phase), Figure 1a, consists of (3x3) domains aligned with the substrate plus (3x3) domains rotated by 30° with respect to the substrate. In addition, some intensity still exists as a 1/3 order ring. The LEED pattern of the higher temperature phase (β phase) is a (3x3) aligned with the substrate. The transition temperature $T_{\alpha \rightarrow \beta}$ is coverage dependent. $T_{\alpha \rightarrow \beta}$ increases with coverage from a value of $T_{\alpha \rightarrow \beta} \sim 100^\circ\text{C}$ for $\text{C/Pt} \sim 1$ to $T_{\alpha \rightarrow \beta} \sim 150^\circ\text{C}$ for $\text{C/Pt} \sim 1.3$.

Any microscopic explanation for the $\alpha \rightarrow \beta$ transition must explain the driving force for domain formation in the α phase. We propose that the $\alpha \rightarrow \beta$ transition corresponds to an order-disorder transition of the rotational orientation of azulene molecules bound to the Pt with the molecular plane parallel to the surface. Our model of the ordering of azulenes in the α phase is shown in Figure 2. Only one domain (aligned with the substrate) is shown. Two phenomena will exist for such ordered overlayers which will lead to a driving force for domain formation. An ordered domain such as that shown in figure 2 will have a strain field associated with it if the Pt atoms below each azulene are moved even slightly from their clean surface equilibrium positions. The total strain energy of the system can be

minimized by domain formation. This has been postulated recently by King, et. al. as the driving force for domain function in the reconstruction of W(001) following adsorption of N.³ The minimization of the strain energy is balanced by the energy required to form the domain wall as well as the energy required to form the slightly less stable domains rotated by 30° with respect to the Pt. This energy balance results in a finite domain size. Above the transition temperature (β phase) the azulenes are rotationally disordered leading to the (3x3) LEED pattern.

The other, less likely, driving force for domain formation in the α phase is the existence of an electrostatic field associated with the ordered domain. Azulene has a dipole moment of .8 Debye. Since the molecule is not well described by a point dipole model, the molecular dipole will not be totally screened by its image. Thus there will be a field associated with such a domain. The interaction of the fields of neighboring domains may lead to stabilization of domains not aligned with the substrate. This effect will again be balanced by the domain wall energy and the instability of the domains not aligned with the Pt. Modeling this effect with a two point charge model of the molecular dipole indicates that it will be minor compared to the strain energy. However, a sophisticated model is required to totally eliminate this possibility.

Within this model the barrier to rotation of an azulene molecule is on the order of 1 kcal/mole. At present we are

taking LEED intensity data in an attempt to measure the critical exponent for this transition.⁴ A detailed discussion of the strain energy will be included in the publication of these results.

We wish to thank D.L. Mills and J. Lawrence for several discussions.

Figure Captions

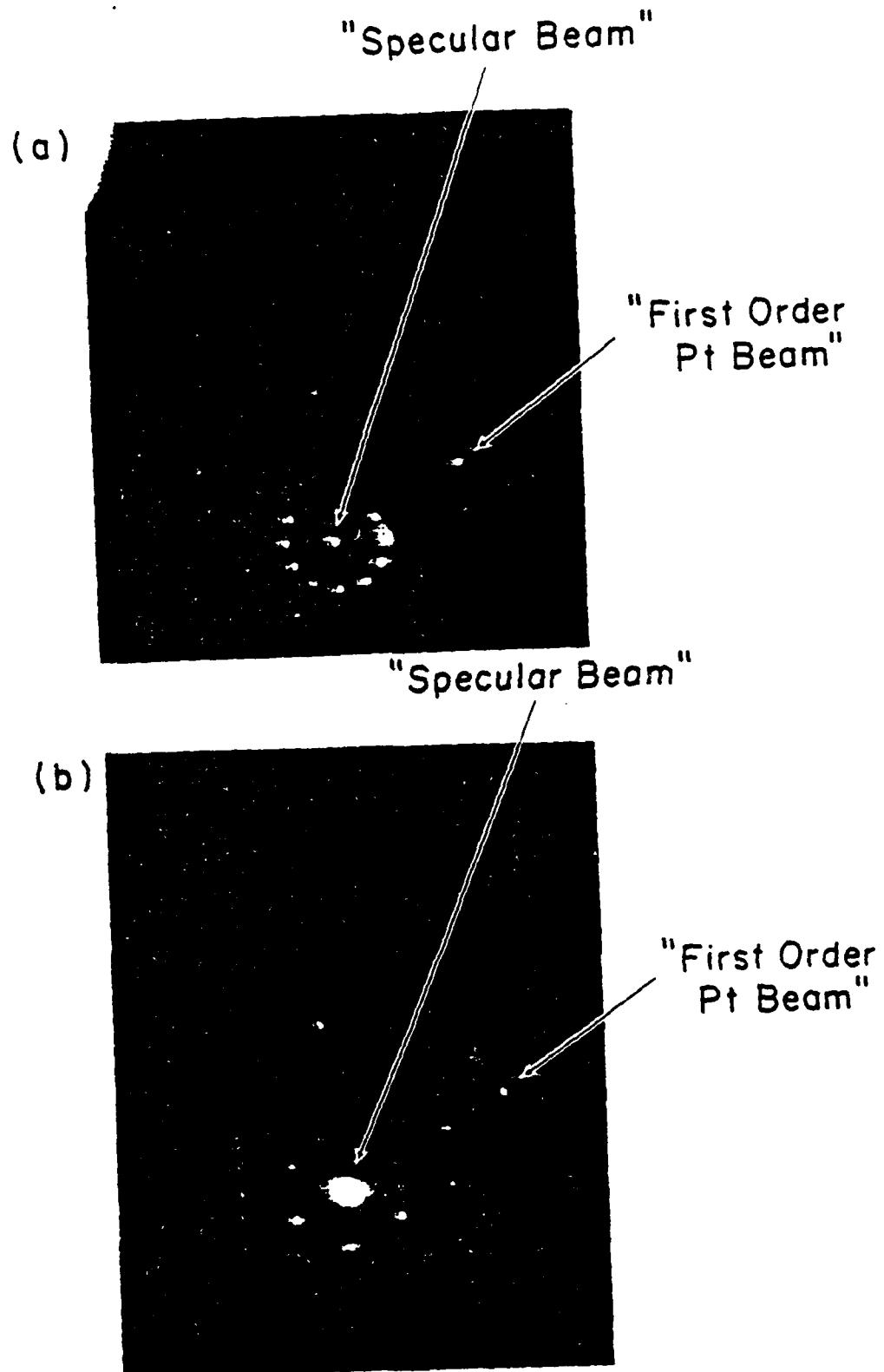
Figure 1

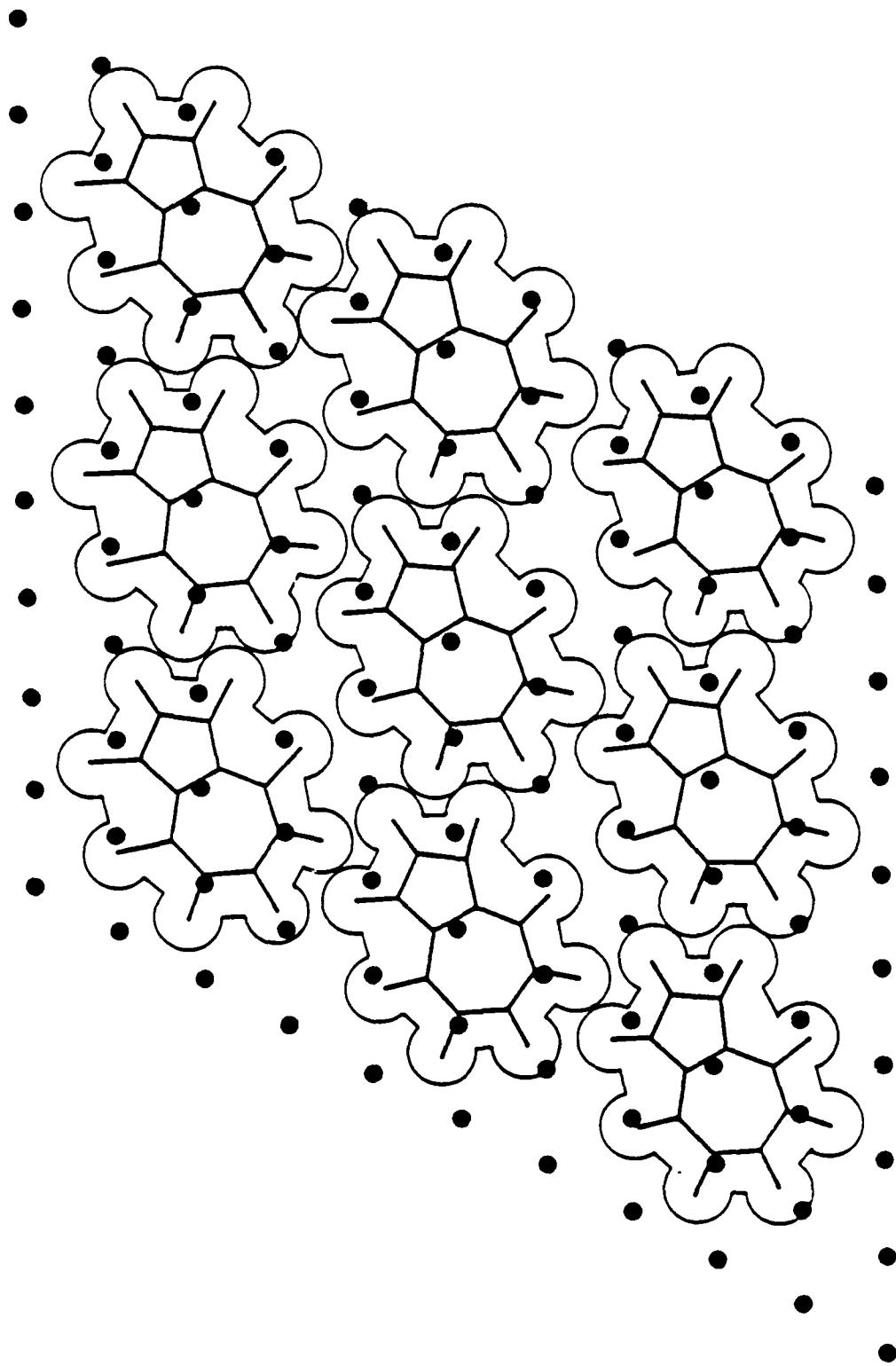
- a) LEED pattern obtained from the α phase of azulene adsorbed on Pt(111).
- b) LEED pattern obtained from the β phase of azulene adsorbed on Pt(111).

Figure 2 Model proposed for the lower temperature (α) phase of azulene adsorbed on Pt(111). Only one domain (aligned with the Pt) is shown. Van der Waal radii are included for the hydrogens to give an indication of the molecular size.

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- a. This work was supported in part by the Office of Naval Research and the Hooker Chemical Corporation Grant of Research Corporation.
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